Additional Thermodynamics Problems

① $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$

For a spontaneous process, $\Delta S_{univ} > 0$. If $\Delta S_{sys} < 0$, ΔS_{surr} is positive and greater than the magnitude of the decrease in ΔS_{sys}.

② (a) ΔS (−) (c) ΔS (−)

(b) ΔS (+) (d) ΔS (+)

③ (a) $CuO_{(s)}$: $42.59 \frac{J}{mol \cdot K}$ $Cu_2O_{(s)}$: $92.36 \frac{J}{mol \cdot K}$

Substances in the solid state have only vibrational motion available to them. The more complex Cu_2O has more vibrational degrees of freedom and a larger standard entropy.

(b) 1 mol $N_2O_{4(g)}$: 304.3 J/K 2 mol $NO_{2(g)}$: $2mol(240.45 \frac{J}{mol \cdot K}) = 480.90 J/K$

More particles have a greater number of arrangements.

(c) $SiO_{2(s)}$: $41.84 \frac{J}{mol \cdot K}$ $CO_{2(g)}$: $213.6 \frac{J}{mol \cdot K}$

Molecules in the gas phase have a larger volume and more motional freedom than those in the solid state. SiO_2 is a covalent network solid so its molecular motion is even more restrained than typical molecular solid.

(d) $CO_{(g)}$: $197.9 \frac{J}{mol \cdot K}$ $CO_{2(g)}$: $213.6 \frac{J}{mol \cdot K}$

The more complex CO_2 molecule has more vibrational degrees of freedom and a slightly higher entropy.

(4) (a) $\Delta S^\circ = (2\ mol \times 192.5 \frac{J}{mol \cdot K}) - [(1\ mol \times 238.5 \frac{J}{mol \cdot K}) + (1\ mol \times 130.58 \frac{J}{mol \cdot K})]$

$\Delta S^\circ = 15.9\ J/K$

↖ small because there are the same moles of gases in the reactants and products. Positive because NH_3 has more degrees of freedom than H_2.

(b) $\Delta S^\circ = (1\ mol \times 122.5 \frac{J}{mol \cdot K}) - [(1\ mol \times 64.67 \frac{J}{mol \cdot K}) + (1\ mol \times 205.0 \frac{J}{mol \cdot K})]$

$\Delta S^\circ = -147.2\ J/K$

↳ Negative because there are fewer (no) moles of gas in the products.

(c) $\Delta S^\circ = [(1\ mol \times 89.6 \frac{J}{mol \cdot K}) + (2\ mol \times 69.91 \frac{J}{mol \cdot K})] - [(1\ mol \times 63.24 \frac{J}{mol \cdot K}) + (2\ mol \times 186.69 \frac{J}{mol \cdot K})]$

$\Delta S^\circ = -207\ J/K$

↳ Negative because there are fewer (no) moles of gas in the products.

(d) $\Delta S^\circ = (1\ mol \times 237.6 \frac{J}{mol \cdot K}) - [(1\ mol \times 197.9 \frac{J}{mol \cdot K}) + (2\ mol \times 130.58 \frac{J}{mol \cdot K})]$

$\Delta S^\circ = -221.5\ J/K$

↳ Negative because there are fewer moles of gas in the products.

(5) (a) $\Delta G^\circ_{Rx} = (2\,mol \times -16.66\ KJ/mol) - [(1\,mol \times 159.4\ KJ/mol) + (1\,mol \times 0\ KJ/mol)]$

$\Delta G^\circ_{Rx} = -192.7\ KJ$

$\Delta H^\circ_{Rx} = (2\,mol \times -46.19\ KJ/mol) - [(1\,mol \times 95.40\ KJ/mol) + (1\,mol \times 0\ KJ/mol)]$

$\Delta H^\circ_{Rx} = -187.78\ KJ$

from prob #4 $\longrightarrow$ $\Delta S^\circ_{Rx} = 15.9\ J/K = 0.0159\ KJ/K$

$\Delta G^\circ_R = \Delta H^\circ_R - T\Delta S^\circ_R = -187.78\ KJ - (298\ K \times 0.0159\ KJ/K) = -192.5\ KJ$

$\Delta G < 0$ Rx is spontaneous

(b) $\Delta G^\circ_{Rx} = (1\,mol \times -240.6\ KJ/mol) - [(1\,mol \times 0\ KJ/mol) + (1\,mol \times 0\ KJ/mol)]$

$= -240.6\ KJ$

$\Delta H^\circ_{Rx} = (1\,mol \times -284.5\ KJ/mol) - [(1\,mol \times 0\ KJ/mol) + (1\,mol \times 0\ KJ/mol)]$

$= -284.5\ KJ$

from Prob #4 $\longrightarrow$ $\Delta S^\circ_{Rx} = -147.2\ J/K = -0.1472\ KJ/K$

$\Delta G^\circ_{Rx} = \Delta H^\circ_R - T\Delta S^\circ_{Rx} = -284.5\ KJ - (298\ K \times -0.1472\ KJ/K) = -240.6\ KJ$

$\Delta G < 0$ Rx is spontaneous.

(c) $\Delta G^\circ_{Rf} = [(1\ mol \times -592.1\ KJ/mol) + (2\ mol \times -237.13\ KJ/mol)] - [(1\ mol \times -833.7\ KJ/mol) + (2\ mol \times -95.27\ KJ/mol)]$

$\Delta G^\circ_{Rf} = -42.1\ KJ$

from probl. #4 $\rightarrow \Delta S^\circ_{Rf} = -207\ J/K = -0.207\ KJ/K$

$\Delta H^\circ_{Rf} = [(1\ mol \times -641.6\ KJ/mol) + (2\ mol \times -285.83\ KJ/mol)] - [(1\ mol \times -924.7\ KJ/mol) + (2\ mol \times -92.30\ KJ/mol)]$

$\Delta H^\circ_{Rf} = -104.0\ KJ$

$\Delta G^\circ_{Rf} = \Delta H^\circ_{Rf} - T\Delta S^\circ_{Rf} = -104.0\ KJ - (298\ K \times -0.207\ KJ/K) = -42.3\ KJ$

$\Delta G < 0$ Rf is spontaneous.

(d) $\Delta G^\circ_{Rf} = (1\ mol \times -161.9\ KJ/mol) - [(1\ mol \times -137.2\ KJ/mol) + (2\ mol \times 0\ KJ/mol)] = -24.7\ KJ$

$\Delta H^\circ_{Rf} = (1\ mol \times -201.2\ KJ/mol) - [(1\ mol \times -110.5\ KJ/mol) + (2\ mol \times 0\ KJ/mol)] = -90.7\ KJ$

from Prob #4 $\Rightarrow \Delta S^\circ_{Rf} = -221.5\ J/K = -0.2215\ KJ/K$

$\Delta G^\circ_{Rf} = \Delta H^\circ_{Rf} - T\Delta S^\circ_{Rf} = -90.7\ KJ - (298\ K \times -0.2215\ KJ/K) = -24.7\ KJ$

$\Delta G < 0$ Rf is spontaneous.

⑥ $K = e^{-\Delta G^\circ / RT}$ ΔG° values from prob # 5

(a) $\frac{\Delta G^\circ}{RT} = \frac{-192.5\ KJ}{(8.314 \times 10^{-3} \frac{KJ}{mol \cdot K})(298\ K)} = -77.7$

$K = e^{-(-77.7)} = 6 \times 10^{33}$ $K >> 1$ Products favored

(b) $\frac{\Delta G^\circ}{RT} = \frac{-240.6\ KJ}{(8.314 \times 10^{-3} \frac{KJ}{mol \cdot K})(298\ K)} = -97.1$

$K = e^{-(-97.1)} = 1 \times 10^{42}$ $K >> 1$ Products favored

(c) $\frac{\Delta G^\circ}{RT} = \frac{-42.3\ KJ}{(8.314 \times 10^{-3} \frac{KJ}{mol \cdot K})(298\ K)} = -17.1$

$K = e^{-(-17.1)} = 3 \times 10^{7}$ $K >> 1$ Product favored

(d) $\frac{\Delta G^\circ}{RT} = \frac{-24.7\ KJ}{(8.314 \times 10^{-3} \frac{KJ}{mol \cdot K})(298\ K)} = -9.97$

$K = e^{-(-9.97)} = 2.1 \times 10^{4}$ $K >> 1$ Products favored